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Equivalence of Donor and Acceptor Fits of Temperature-Dependent Carrier-Concentration Data

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It is shown that the usual charge-balance analysis of temperature-dependent carrier-concentration data cannot distinguish between the donor and acceptor behavior of a center which is emitting carriers to a particular band, even though the statistics are different in the two cases. Other data, such as mobility or analytical results are needed to make the distinction.

We consider an n-type semiconductor sample, e.g., GaAs, which contains shallow donors, shallow acceptors, and deep donors of concentration N_{DS}, N_{AS}, and N_{DD}, respectively, with the shallow levels ionized at all temperatures of interest. Then, for $n \gg p$, the standard charge-balance analysis, using Boltzmann statistics, gives[1,2]

$$n + N_{AS} = [N_{DD}/(1 + n/\phi_{DC})] + N_{DS} , \tag{1}$$

where

$$\phi_{DC} = (g_{D0}/g_{D1}) N'_C T^{3/2} \exp(-E_{DC}/kT) .$$

Here, $N'_C = 2(2\pi m_n^* k)^{3/2}/h^3$, E_{DC} is the absolute-energy difference (activation energy) between the deep donor and the conduction band, g_{D0} (g_{D1}) is the degeneracy of the unoccupied (occupied) deep donor level and all other constants have their usual meanings. Exactly the same form of equation results if we consider a deep acceptor, emitting holes to the valence band.[2] Then, for $p \gg n$,

$$p + N_{DS} = [N_{AA}/(1 + p/\phi_{AV})] + N_{AS} , \tag{2}$$

where

$$\phi_{AV} = (g_{A1}/g_{A0}) N'_V T^{3/2} \exp(-E_{AV}/kT) .$$

Here, E_{AV} is the activation energy with respect to the valence band. Thus, except for the flip of the degeneracy factor, statistics for acceptors emitting holes to the valence band are exactly the same as those for donors emitting electrons to the conduction band. This fact is well known and causes no confusion.

What can cause confusion, however, is the case of a deep acceptor (donor) emitting electrons (holes) to the conduction (valence) band. The problem here is that a level relatively near the conduction (valence) band is naturally assumed to be a donor (acceptor), but such an assumption is not necessarily correct.[3] Consider the case of an acceptor emitting electrons to the conduction band, as depicted in Fig. 1(b). (Note that acceptors can emit the electrons received from shallower donors.) It can easily be shown[2] that the charge-balance equation gives

$$n + N_{AS} + [N_{AA}/(1 + \phi_{AC}/n)] = N_{DS} , \tag{3}$$

where

$$\phi_{AC} = (g_{A0}/g_{A1}) N'_C T^{3/2} \exp(-E_{AC}/kT) .$$

This equation is not equivalent to Eq. (1), so that it seems reasonable that a fit of n vs T should distinguish between the two. The point of this note is that the fit *cannot* distinguish between the donor [Eq. (1)] and acceptor [Eq. (3)] cases.

We write Eq. (1) as

$$n^2 + n[\phi_{DC}^{(d)} + (N_{AS} - N_{DS})^{(d)}] + \phi_{DC}^{(d)}[(N_{AS} - N_{DS})^{(d)} - N_{DD}^{(d)}] = 0 , \tag{4}$$

where the superscript (d) denotes the donor fit. Similarly, Eq. (3), the "acceptor" fit becomes

$$n^2 + n[(N_{AS} - N_{DS})^{(a)} + \phi_{AC}^{(a)} + N_{AA}^{(a)}] + \phi_{AC}^{(a)}(N_{AS} - N_{DS})^{(a)} = 0 . \tag{5}$$

The form of both equations is $n^2 + bn + c = 0$ and, furthermore, the general temperature dependencies of $b^{(a)}$ and $c^{(a)}$ are identical to those of $b^{(d)}$ and $c^{(d)}$, respectively, so that a least-squares computer solution of n vs T will give $b^{(a)} = b^{(d)}$ and $c^{(a)} = c^{(d)}$ at every temperature. Thus,

$$\phi_{DC}^{(d)} + (N_{AS} - N_{DS})^{(d)} = (N_{AS} - N_{DS})^{(a)} + \phi_{AC}^{(a)} + N_{AA}^{(a)} , \tag{6a}$$

$$\phi_{DC}^{(d)}[(N_{AS} - N_{DS})^{(d)} - N_{DD}^{(d)}] = \phi_{AC}^{(a)}(N_{AS} - N_{DS})^{(a)} . \tag{6b}$$

By taking a temperature derivative of Eq. 6(a) we get $d\phi_{DC}^{(d)}/dT = d\phi_{AC}^{(a)}/dT$, or $\phi_{DC}^{(d)} = \phi_{AC}^{(a)} + K$. But at very low temperature, ϕ_{DC}, $\phi_{AC} \to 0$, so that $K = 0$. Therefore, $\phi_{DC}^{(d)} = \phi_{AC}^{(a)}$, and their respective terms cancel in Eq. 6(a) and 6(b). By subtracting Eq. 6(b) from Eq. 6(a), we get the final relationships:

$$N_{AA}^{(a)} = N_{DD}^{(d)} , \tag{7a}$$

$$(N_{AS} - N_{DS})^{(a)} = (N_{AS} - N_{DS})^{(d)} - N_{DD}^{(d)} . \tag{7b}$$

Also, from $\phi_{DC}^{(d)} = \phi_{AC}^{(a)}$, it is clear that $E_{DC}^{(d)} = E_{AC}^{(a)}$. Thus, the computer fit of n vs T gives the same concentration for the deep level, whether it is assumed to be a donor or an acceptor. The compensating centers, N_{DS} and N_{AS}, will not

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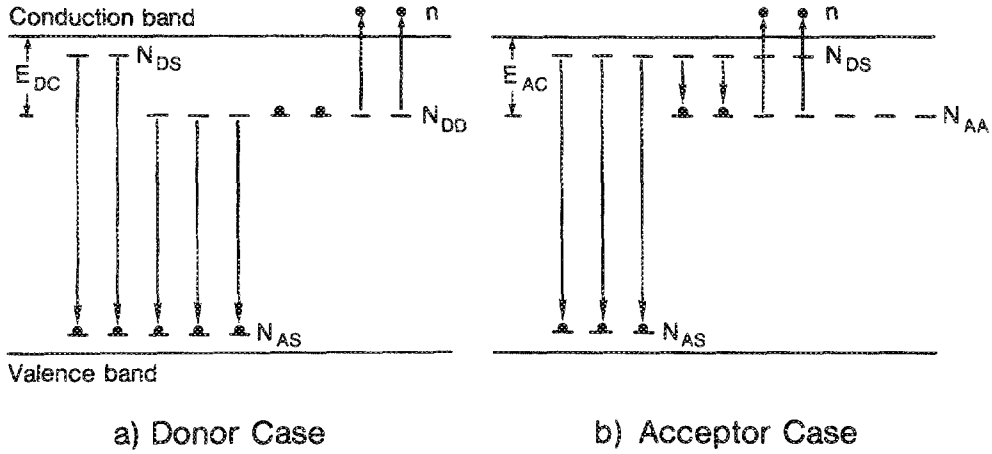

FIG. 1. Schematic illustration of two cases for which the various donor and acceptor concentrations give identical free electron concentrations. Case (a): deep donor; case (b): a deep acceptor.

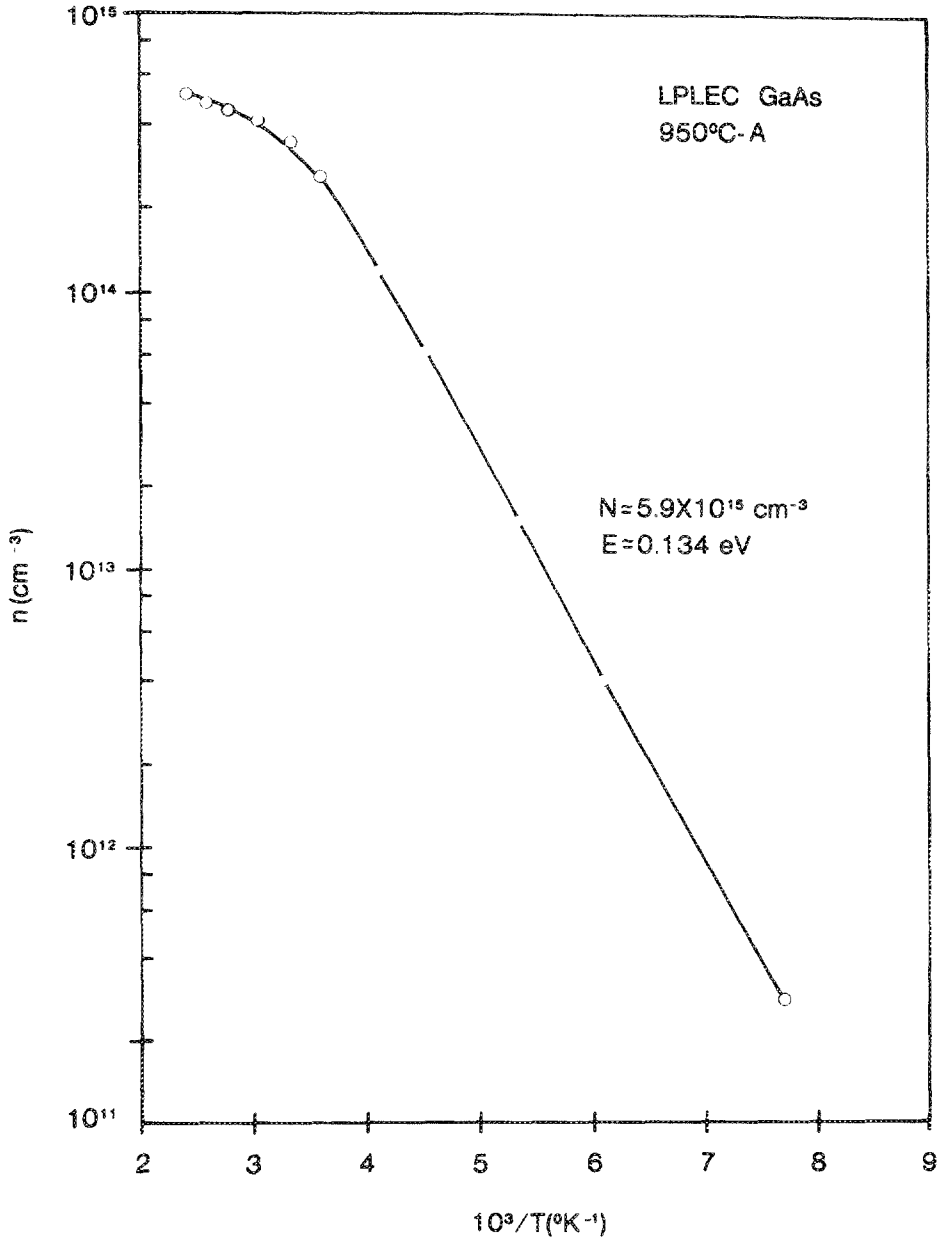

FIG. 2. Carrier concentration vs inverse temperature for a low-pressure LEC GaAs crystal annealed at 950 °C for 5 h in an evacuated quartz tube.

TABLE I. Comparison of donor and acceptor fits.

Fit	E_{DC} (eV)	E_{AC} (eV)	N_{DD} (cm^{-3})	N_{AA} (cm^{-3})	$N_{AS}-N_{DS}$ (cm^{-3})
Donor	0.134	···	5.9×10^{15}	···	5.3×10^{15}
Acceptor	···	0.134	···	5.9×10^{15}	-0.6×10^{15}

be equal, of course. The whole situation is illustrated in Fig. 1.

One might then ask how the donor and acceptor cases can be distinguished. Analytical techniques, such as secondary ion mass spectroscopy (SIMS), are useful if the electrical activity of most of the common impurities is known. That is, for the donor case to be correct, $N_{AS} > N_{DS}$, and for the acceptor case, $N_{AS} < N_{DS}$. Further information can be obtained from mobility data, especially if low-temperature data, which are sensitive to the ionized-impurity concentration, N_I, can be obtained. For the donor case, $N_I^{(d)} = 2N_{AS} + n$, while for the acceptor case, $N_I^{(a)} = 2N_{DS} - n$. It is possible that only one of these relationships may be consistent with the corresponding n vs T fit.

Finally, the relationships (7a) and (7b) can be useful in that if one of the equations [Eqs. (1) or (3)] is fitted, the results for the other case are obtained immediately. An example is given in Fig. 2 and Table I, where the energies are with respect to the conduction band. From SIMS data, the total concentration of all common shallow donors (Si, S, and Se) is about 2×10^{15} cm^{-3}. Therefore, from Table I, the donor fit gives $N_{AS} \simeq 7\times10^{15}$ cm^{-3}, and the acceptor fit, $N_{AS} \simeq 1\times10^{15}$ cm^{-3}, where N_{AS}, in this case, includes all acceptors below $E_C - 0.13$ eV. Since the Mg and Fe concentrations alone total about 3×10^{15} cm^{-3}, according to SIMS, it appears that the donor case is more reasonable. Mobility data support this assignment, although inhomogeneous current conduction can sometimes give an artificially low mobility.[4]

In summary, we have tried to point out that a relatively deep (nonhydrogenic) level may not *a priori* be declared a donor or acceptor simply because it is close to the conduction or valence bands, respectively, and that the usual statistical analysis of temperature-dependent carrier-concentration data can also, by itself, not distinguish between the two cases. Although this latter fact follows from a rather trivial analysis, it appears to not be generally realized at this time. The analysis also gives the relationships between the various parameters in the two cases.

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[2]D. C. Look, in *Semiconductors and Semimetals, Vol. 19*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1983), pp. 156–158.
[3]See, e.g., M. R. Lorenz, B. Segall, and H. H. Woodbury, Phys. Rev. **134**, A751 (1964).
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Surface-energy-driven grain growth during rapid thermal annealing (<10 s) of thin silicon films

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Surface-energy-driven grain growth in 70-nm-thick phosphorus-doped Si films is reported for anneals of less than 10 s over a temperature range of ~1100 to 1225 °C. Secondary grains grow to sizes of 1 μm or larger and have (111) crystallographic texture, indicating surface energy minimization. A kinetic analysis of grain growth suggests that while the rate of grain boundary motion is limited by P diffusion, the initial growth rate can be high, 72 nm/s at 1100 °C.

Normal grain growth in polycrystalline thin films usually results in randomly oriented columnar grains with diameters of the order of the film thickness. In some cases a minor fraction of the grains undergoes further growth at the expense of the other normal grains in what is called *abnormal* or *secondary* grain growth. The factor which provides selectivity, determining which grains become large secondary grains, can be surface energy anisotropy and hence secondary grain growth is enhanced by the large surface-to-volume ratio of very thin films. That is, the total energy of the system can be minimized by growth of grains with orientations that minimize the surface energy and which consume normal grains that have higher surface energies. This process is termed surface-energy-driven grain growth (SEDGG). The driving force due to surface energy anisotropy persists until all secondary grains impinge and all normal grains are con-

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